

Temperature fitting of partially resolved rotational spectra

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Temperature fitting of partially resolved rotational spectra

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ABSTRACT: In this paper we present a method to automatically fit the temperature of a rotational spectrum. It is shown that this fitting method yields similar results as the traditional Boltzmann plot, but is applicable in situations where lines of the spectrum overlap. The method is demonstrated on rotational spectra of nitric oxide from an atmospheric pressure microwave plasma jet operated with a flow of helium and air, obtained with two different methods: laser induced fluorescence and optical emission spectroscopy. Axial profiles of the rotational temperatures are presented for the ground NO *X* state and the excited NO *A* state.

KEYWORDS: Data processing methods; Plasma diagnostics - interferometry, spectroscopy and imaging

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1 Introduction

The rotational spectrum of a species is a valuable data source for determining gas temperatures inside a plasma. The most common method is a Boltzmann plot, where the peak intensities of the rotational lines are plotted logarithmically against the energy of the rotational transition. Since the line intensities follow a Boltzmann distribution, the slope of the points is equal to $1/k_B T$, where k_B is Boltzmann's constant, and T the temperature [1]. Several methods exist based on Boltzmann plots to determine temperatures with the intensities of one, two or more rotational lines [2–4].

A Boltzmann plot is insightful, because deviations from the Boltzmann distribution are easily observed if points deviate from the linear fit [5]. Furthermore the method does not require a lot of computational power. The difficulty arises in the determination of the peak intensities. Since this is usually done by hand, or by taking the local maxima of a spectrum. This requires that the width of the instrumental profile of the measurement device is much smaller than the spectral distance between the rotational lines. Furthermore, when the number of data points per peak is small, a fitting procedure needs to be applied to obtain the peak maxima. This can also induce additional uncertainties.

Overlapping spectra can lead to inaccuracies in Boltzmann plots. Especially for molecules with relative high mass such as NO and N₂ the rotational lines are close together — typically in the order of a few pm — as the energy difference between the levels increases with decreasing reduced mass of the rotator. This puts high demands on the used spectrometer. Partially overlapping spectra can even occur in LIF measurements as the FWHM of dye lasers is typically of the order of 2 pm.

In cases where Boltzmann plots are not applicable, temperature determination is often done using software packages that calculate rotational spectra. Examples of such software are Lifbase from Luque et al. [6], Specair from Laux [7], and Lifsim from Bessler et al. [8]. These programs perform calculations of spectra similar as shown in this paper. However, the temperature is always an input parameter, and these programs do not yield automatically the best fit to a measured

spectrum. In literature several examples exist of temperatures that are determined by fitting. For example for NO a method is derived from Lifsim by Bessler et al. [9]), for N_2^+ a fitting method is presented by Linss et al. [10], and for N_2 , O_2 , OH and NO by Andre et al. [11]. However finding a temperature is still often done manually by fitting the spectrum by eye. This is a subjective method, and leads to serious inconsistencies often found in scientific papers on the accuracy of the gas temperature, which is often overestimated.

In the next section we propose a method to determine the rotational temperature automatically by fitting a spectrum directly to the measured spectrum with a least-square method. The instrumental profile is incorporated into the fitting method, making it possible to fit spectra with overlapping lines, lines from different rotational branches, and implement a background correction. In section 4 we apply our method to rotational spectra of nitric oxide (NO), obtained with Optical Emission Spectroscopy (OES) and Laser Induced Fluorescence (LIF).

2 Fitting method

Temperature determination is most often made by rotational spectra obtained from OES and LIF. We describe briefly the procedure below:

2.1 OES

For OES the light emitted by the plasma is measured with a spectrometer. For temperature determination we only need the relative intensities, and we consider rotational states from a single vibrational band. This means that we only have to consider factors which depend on the rotational state. The intensity I_i of a line of transition i is reduced to,

$$I_i \propto A_i \cdot (2J_i + 1) e^{-\frac{E_i}{k_B T}} \quad (\text{OES}) \quad (2.1)$$

where A_i is the Einstein emission coefficient for transition i . J_i and E_i represent the rotational number and energy of the emitting (upper) state of the transition i . The $2J_i + 1$ factor is to account for the degeneracy of the rotational states, where J_i is the rotational quantum number of emitting (upper) state of the transition i . The temperature dependence is included in a Boltzmann exponent, which means that this method is physically equivalent to a Boltzmann plot. E_i is the energy of the rotational state, given by,

$$E_i = B_v \cdot J_i(J_i + 1) \quad (2.2)$$

where B_v is the rotational constant. Higher order terms represent a fraction less than 1% for $J_i < 40$ for most species [12], and can thus be neglected in many cases.

2.2 LIF

In the case of LIF the spectrum is measured by scanning a dye laser along rotational transitions. The fluorescence signal is often a broadband signal as a spectrometer with open slit or a interference filter (typically passing 10 nm) is used, such that all rotational transitions from one vibrational band are detected.

LIF is a two-step process: first a photon is absorbed, followed by emission of the populated level. After Uddi et al. [13] the intensity I_i of a line of transition i can be written as,

$$I_i \propto \frac{A_{\nu'}^{v''}}{Q + \sum_{\nu''} A_{\nu'}^{v''}} \cdot B_i \cdot (2J_i + 1) e^{-\frac{E_i}{k_B T}} \quad (2.3)$$

where B_i is the Einstein absorption coefficient for transition i , induced by the laser. $A_{\nu'}^{v''}$ is the Einstein emission coefficient for the detected vibrational transition, divided by the sum over all vibrational states, plus the quenching coefficient Q . Since this A coefficient is independent of the transition i , equation (2.3) can be reduced to,

$$I_i \propto B_i \cdot (2J_i + 1) e^{-\frac{E_i}{k_B T}} \quad (LIF) \quad (2.4)$$

This equation is valid if: 1. The laser intensity is low and there is no saturation, i.e. stimulated emission can be neglected; 2. Vibrational energy transfer is negligible, or at least independent of the rotational state; 3. Rotational energy transfer is faster than the lifetime of the excited state, such that there is a redistribution of the rotational levels of the excited state; 4. Quenching is independent of the rotational state; 5. The plasma is optically thin, i.e. the absorbed laser energy is negligible compared to the total laser energy.

To calculate the total spectrum $S(\lambda)$, the line intensities have to be multiplied with a line profile $g(\lambda)$ and summarized. We also add a constant background C ,

$$S(\lambda) = C + \sum_i I_i \cdot g(\lambda - \lambda_i) \quad (2.5)$$

The line profile is an arbitrary function, composed of the spectral distribution function of the transition, and the laser profile (in case of LIF) or the instrumental profile of the spectrometer (in case of OES). In most cases the line profile can be adequately approximated by a Voigt profile,

$$g(\lambda) = G(\lambda, \Delta_G) \otimes L(\lambda, \Delta_L) \quad (2.6)$$

where G is a Gaussian curve with width Δ_G and L is a Lorentzian curve with width Δ_L .

Of the above quantities A_i , B_i , λ_i , J_i and B_v are species properties, which are published for many species. Assuming these quantities are known, the resulting spectrum function is $S(\lambda; I_0, T, C, \Delta_G, \Delta_L)$. This function can be programmed into a computer and fitted to a measured spectrum, with λ as independent parameter and I_0 , T , C , Δ_G and Δ_L as fitting parameters. We used MATLAB to perform the fitting, in particular the function FIT, which is part of the CURVE FITTING TOOLBOX. This function performs a least-square fit, and has the ability to calculate confidence intervals on the fitting parameters. It is possible to determine C , Δ_G and Δ_L with other experimental methods, which reduces the number of fitting parameters to two.

3 Experimental setup

The fitting method described in the previous section is applied rotational spectra of nitric oxide (NO), obtained with OES and LIF.

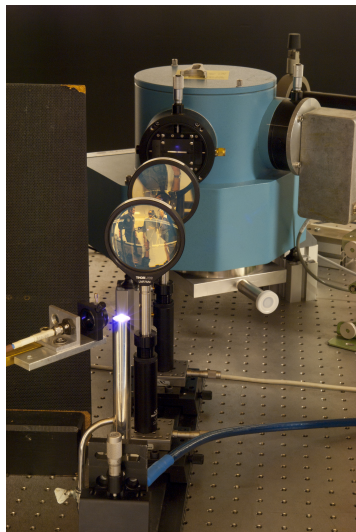


Figure 1. Picture of the atmospheric pressure microwave helium jet, with the collecting fiber for OES on the foreground, and the LIF detection system on the background.

The NO source is an atmospheric pressure microwave plasma jet, as described by Hrycak et al. [14] (see figure 1). The input microwave power is 30 W. The plasma is operated with a flow of a 6.0 slm helium mixed with 0.2 slm of air, resulting in a flow speed of approximately 1 m/s. The tube ends in ambient air.

The OES measurements are performed using a 1 m Jobin Yvon spectrometer with a SBIG CCD camera, with an instrumental profile width of approximately 25 pm, and a spectral distance between pixels of 6 pm. The light is collected using a lens and a fiber, which provides a spot size in the plasma of 2 mm diameter. The measured spectrum is around 247 nm, which corresponds to the transition $\text{NO } A^2\Sigma^+ - X^2\Pi (v = 0 - 2)$.

The LIF measurements are performed with a Sirah dye laser, pumped with an Edgewave Nd:YAG laser at 355 nm and a repetition rate of 4 kHz. The dye laser beam is frequency doubled, resulting in a UV beam around 226 nm, and 10 μJ per pulse, with a line width of 1.4 pm. The laser excites the $\text{NO } X^2\Pi - A^2\Sigma^+ (v = 0 - 0)$ transition. The detection system consists of a McPherson EUV monochromator and a Hamamatsu R8486 photomultiplier connected to a counting system. The monochromator is set at 247 nm with a wide exit slit of 1 mm and a FWHM of 10 nm, such that all rotational transitions from the $\text{NO } A^2\Sigma^+ - X^2\Pi (v = 0 - 2)$ vibrational transition are detected. The laserbeam is not focussed, in order to avoid saturation. The size of the laser beam and the optics that focus the LIF signal onto the entrance slit of the monochromator make that the measurements have a detection volume of approximately 1 mm^3 .

4 Applying the fitting method

Figure 2 shows an example of a LIF spectrum of NO. To determine the rotational temperature we applied the fitting method described in section 2. The rotational energy transfer rate for the NO A state is in the order $10^{10} \text{ cm}^3\text{s}^{-1}$ for helium [15] and air [16]. For atmospheric pressure RET is in the order of 1 ns, while the measured decay time of the excited state is 48 ns, thus the assumption

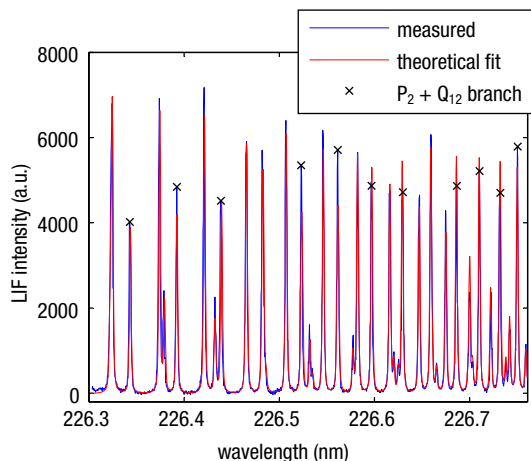


Figure 2. Rotational spectrum of NO, obtained with LIF inside the plasma jet at 3 mm above the tube end. The theoretical spectrum is plotted, with a fitted values $T_{rot} = 860 \pm 43$ K, $\Delta_G = 2.2 \pm 0.3$ pm and $\Delta_L = 1.0 \pm 0.2$ pm.

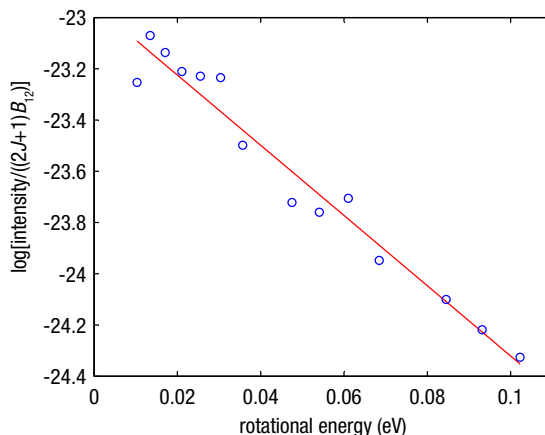


Figure 3. Boltzmann plot of a LIF measurement of NO inside the plasma jet at 3 mm above the tube end. The used lines are indicated with \times in figure 2. The linear fit gives a temperature of $T_{rot} = 846 \pm 106$ K.

that the rotational states are redistributed in the excited state is justified. Vibrational transfer is much slower [17], and can be neglected.

From Lifbase [6, 18] we obtained the parameters B_i (for the NO $X - A$ ($v = 0 - 0$) transitions), λ_i and J_i (for the NO X ($v = 0$) state) for each line in the spectrum. Furthermore $B_v = 1.6961 \text{ cm}^{-1}$ [12]. The fitted spectrum is shown in figure 2, with a fitted temperature of $T_{rot} = 860 \pm 43$ K. The error margin is a 95% confidence interval as provided by the MATLAB FIT function.

From the same LIF measurement lines from the P_2 branch and the overlapping Q_{12} branch are used to make a Boltzmann plot (see figure 3). The corresponding temperature is calculated to be $T_{rot} = 846 \pm 106$ K (95% confidence interval).

Results from the OES measurement are shown in figure 4. In this case the resolution of the spectrum is insufficient to completely resolve the rotational lines. Consequently, making

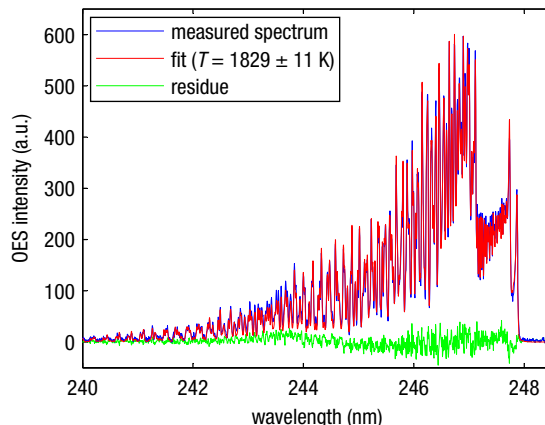


Figure 4. Rotational spectrum of NO, obtained with OES from inside the plasma jet at 3 mm above the tube end. The theoretical spectrum is plotted, with a fitted values $T_{rot} = 1829 \pm 11$ K, $\Delta_G = 24.6 \pm 0.8$ pm and $\Delta_L = 8.1 \pm 0.5$ pm.

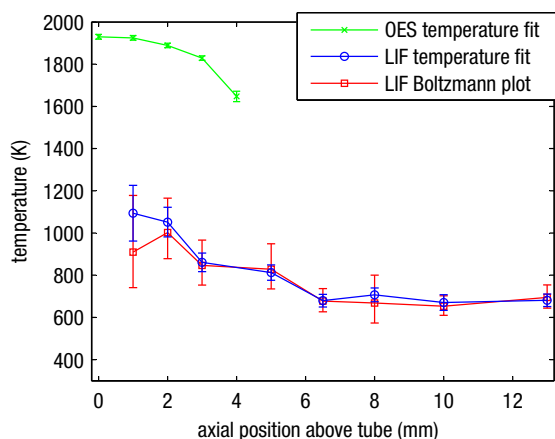


Figure 5. Axial temperature profiles obtained with different methods.

a Boltzmann plot is not possible. The temperature fitting, however, is still applicable. The parameters A_i (for the NO $A - X$ ($v=0-2$) transitions), λ_i and J_i (NO A ($v=0$)) are obtained from Lifbase [6, 18], and $B_v = 1.9862 \text{ cm}^{-1}$ [12]. The resulting temperature is $T_{rot} = 1829 \pm 11$ K (95% confidence interval).

Similar OES and LIF measurements are performed at different axial positions in and above the plasma. The axial temperature profiles are shown in figure 5. The temperatures from the Boltzmann plot and the fitting method correspond within the margin of error, where the fitting method has the smallest error margins. While the LIF signal from the NO X ground state is still measurable in the afterglow of the plasma, the emission from the NO A excited state can only be measured inside the plasma.

The OES temperatures from the NO A excited state are higher than the LIF temperatures from the NO X ground state. Larger rotational temperatures than the gas temperature for NO A is common, see for example Staack et al. [19]. This can be explained by the formation process (most probably the association process) causing specific large rotational excitation, while due to

the limited rotational life time of the excited state equilibration with the gas temperature is not possible. In the case of ground state NO, the lifetime is much larger and thus the NO X rotational temperature is a better estimate of the gas temperature.

5 Conclusions

We present a method to automatically fit a rotational temperature to a measured spectrum. Because the line positions and Einstein coefficients are taken from literature, the method is relatively simple. The temperature fitting works well in situations where a Boltzmann plot is not applicable due to overlapping lines. We applied the method to rotational spectra of NO in an atmospheric pressure plasma jet. The fitted temperatures are $T_{rot} = 860 \pm 43$ K for NO in the $X^2\Pi$ ground state (measured with LIF), and $T_{rot} = 1829 \pm 11$ K for NO in the $A^2\Sigma^+$ excited state.

To obtain MATLAB scripts that implement the described fitting method, please contact the authors.

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